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Acetic acid and lithium chloride effects on hydrothermal carbonization of lignocellulosic biomass

Joan G. Lynam, Charles J. Coronella *, Wei Yan, Mohammad T. Reza, Victor R. Vasquez

Department of Chemical & Materials Engineering, University of Nevada, Reno, 1664 N. Virginia St., MS0170, Reno, NV 89557, USA

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ABSTRACT

As a renewable non-food resource, lignocellulosic biomass has great potential as an energy source or feedstock for further conversion. However, challenges exist with supply logistics of this geographically scattered and perishable resource. Hydrothermal carbonization treats any kind of biomass in 200 to 260 °C compressed water under an inert atmosphere to produce a hydrophobic solid of reduced mass and increased fuel value. A maximum in higher heating value (HHV) was found when 0.4 g of acetic acid was added per g of biomass. If 1 g of LiCl and 0.4 g of acetic acid were added per g of biomass to the initial reaction solution, a 30% increase in HHV was found compared to the pretreatment with no additives, along with greater mass reduction. LiCl addition also reduces reaction pressure. Addition of acetic acid and/or LiCl to hydrothermal carbonization each contribute to increased HHV and reduced mass yield of the solid product.

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1. Introduction

Energy independence has been a goal in the United States since the oil crisis in the 1970's. Interest in "homegrown" fuels has fluctuated directly with the price of imported non-renewable fuels. However, using potential food, such as corn, to produce energy seems unethical in a world of limited caloric resources. As a non-food renewable resource, lignocellulosic biomass could be used as an important starting point to produce biofuels indefinitely. Enhanced biofuels can be produced from low-value biomass via two methods. With biochemical conversion, biomass is broken down by enzymatic or chemical processes and then converted to ethanol through fermentation. In thermochemical conversion, biomass is broken down to intermediates using heat and upgraded to fuels using both heat and pressure with catalysts present. However, lignocellulosic biomass exists in many diverse forms. Crops such as hard or soft woods, switch grass, or miscanthus can be grown, while waste products from food production, such as rice hulls, corn stover, straws, and bagasse, can be obtained easily and cheaply. The great variation in solids handling for these different feedstocks causes difficulties in further processing. Also, the seasonal nature of these plant-based materials requires good storage properties. Pretreating biomass by heating it in an inert environment can improve the usefulness of these feedstocks (Prins et al., 2006a,b; Yu et al., 2008). Pretreatment can be performed as a dry process or as a wet process. The dry process is called dry torrefaction or mild pyrolysis. When done in hot compressed water, the process is often referred to as wet torrefaction, biomass hydrolysis, or hydrothermal carbonization. Relatively simple processes, both pretreatments increase not only a biomass's density to decrease transportation costs, but also its hydrophobic behavior for simpler storage. Torrefaction's solid product is easily crushable, regardless of the particular initial feedstock, leading to a more uniform feed for processing. In addition, the process improves the solid product's heating value on a weight basis, with increased carbon percentage, making it more suitable for co-firing in coal power plants. Although pretreatment produces some carbon dioxide, carbon is taken from the atmosphere and fixed in the original biomass, so the process is carbon neutral.

Dry torrefaction typically is performed between 225 and 300 °C with reaction times of between 30 min and several hours (Prins et al., 2006a,b; Sadaki and Negi, 2009). Wet torrefaction or hydrothermal carbonization is run at slightly lower temperatures (180–260 °C), with liquid water used, necessitating high pressures of up to 4.6 MPa gauge. The reactions involved do not proceed significantly at temperatures lower than 180 °C. Although reaction time for hydrothermal carbonization can be several hours, the initial 20 min appear to generate the vast majority of product (Knezevic et al., 2010). Hydrothermal carbonization is preferred for several reasons. At temperatures of 227 °C to 327 °C, the ionic product of water is maximized, leading to the possibility that it could act as an acid or base catalyst for reactions. Also, the dielectric constant of water is much lower at these temperatures than ambient temperatures, causing it to behave more like a non-polar solvent (Yu et al., 2008).

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* Corresponding author. Tel.: +1 775 784 4253; fax: +1 775 784 4764.
E-mail address: coronella@unr.edu (C.J. Coronella).

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Hydrothermal carbonization when used at similar temperatures to dry torrefaction is more effective in providing energy densification by reducing the mass of the solid product, and increasing its higher heating value (HHV) (Yan et al., 2009). The characteristics of hydrothermal carbonization, including the shorter reaction time at lower temperature and reduced equilibrium moisture content, which reduces degradation over time, indicate its greater feasibility for a seasonal feedstock (Yan et al., 2009).

Using hydrothermal carbonization, the energy densification ratio, the ratio of the heating value of the pretreated solid fuel product to that of the original biomass, can be increased by 3% to 47%, depending on the type of biomass and reaction conditions. Reaction temperature has been found to be the most significant variable in changing the solid product qualities, with higher temperatures decreasing mass yield and increasing HHV. Biomass pretreated by hydrothermal carbonization has increased fixed carbon and atomic carbon, implying it has become a fuel similar to low rank coal. In addition, reduced equilibrium moisture content in pretreated biomass indicates a more hydrophobic nature leading to better storage properties (Acharjee, 2010).

Hydrothermal carbonization produces not only a solid fuel for use or subsequent conversion, but also other potential high-value products. Glucose, among other simple sugars, and 5-hydroxymethyl furfural (5-HMF) can be precipitated in significant quantities from the aqueous product stream. The aqueous stream also contains volatile acids. For example, when loblolly pine was pretreated at 230 °C for 5 min, 0.025 g of acetic acid was produced per gram of original wood. Formic acid (0.0085 g) and lactic acid (0.0026 g) were produced as well (Yan et al., 2010). These acids lower the pH in the reaction system as they are produced.

The role of pH in hydrothermal carbonization has not been fully explored. The reaction rate at 300 °C for solutions of glucose, which can serve as a model for biomass, was observed at pH levels of 1 to 14, but no clear trends emerged (Knezevic et al., 2009). An initial pH of greater than 7 leads to a liquid rather than solid product (Ando et al., 2000; Hu et al., 2008). Many hydrothermal carbonization processes report the addition of such acids as citric acid (Hu et al., 2008; Titirici and Antonietti, 2007), acrylic acid (Demir-Carkan, 2009), and sulfuric acid (Lu et al., 2009a,b). The effect of acetic acid was chosen for investigation because it is the primary acid produced in hydrothermal carbonization (Yan et al., 2010), thus reducing the complexity of the reaction system. Also, acetic acid could be recycled to treat fresh batches of biomass, minimizing cost. A reaction temperature of 230 °C may be preferable because the degradation of glucose, a valuable product of hydrothermal carbonization, rapidly increases above 230 °C (Yu et al., 2008). In addition, higher temperatures increase the pressure necessary to maintain liquid water, requiring sturdier reactor walls and making the process more hazardous and expensive. It could be expected that adding lithium chloride would reduce pressure in aqueous systems, as well as having a possible catalytic effect and increasing the activity of the [H^+] ions in the system, reducing pH. Thus, investigating the effects of both acetic acid and lithium chloride on the hydrothermal carbonization process at 230 °C was deemed useful.

2. Methods

2.1. Biomass

As a typical lignocellulosic biomass, loblolly pine was acquired from Alabama, USA. On a mass basis, it consists of 11.9% hemicelluloses, 54.0% cellulose, 25% lignin, 8.7% extractives and 0.4% ash (Yan et al., 2010). Pine samples were milled to the desired particle size of 14–28 mesh (1.168–0.589 mm in diameter) before hydrothermal carbonization. Before treatment, the moisture content was measured to be 5.2% by weighing a sample, then measuring weight loss after drying for 24 h at 105 °C.

2.2. Acetic acid

Glacial acetic acid (Sigma–Aldrich, 99.7+%, ACS Reagent) was diluted with deionized water to 0.64 M acetic acid, 1.24 M acetic acid, 1.79 M acetic acid, and 2.31 M acetic acid. The solutions had pH values of 2.48, 2.31, 2.25, and 2.17.

2.3. Lithium chloride

Lithium chloride (Alfa Aesar, anhydrous, 99% min, −20 mesh) was dissolved by stirring into deionized water resulting in either a 4.40 M or a 7.95 M LiCl solution. Thus, either 1 or 2 g of LiCl was added per g of pine for a reaction. For the runs where both LiCl and acetic acid were present, LiCl was stirred into the 1.24 M acetic acid solution so that 1 g of LiCl was added per g of pine. Lithium chloride is extremely soluble in water. The solubility is 0.8 g LiCl/g water at 22 °C, and 1.7 g LiCl/g water at 230 °C (Monnin et al., 2002). Since the Parr reactor used did not have a stirrer, a uniform solution could not be guaranteed, unless the LiCl was able to be dissolved at room temperature. Using 2 g LiCl per g of pine was about half of the solubility limit at 22 °C.

2.4. Hydrothermal carbonization

Hydrothermal carbonization of loblolly pine was performed in a Parr Series 4560 bench-top reactor of volume 100 mL (Moline, IL). For each run, loblolly pine was placed in the reactor and either deionized water (as the control), an acetic acid solution, a LiCl solution, or the combination solution was poured in the reactor to cover the biomass. In all runs, water to loblolly pine mass ratio was 5:1. A glass liner was placed in the reactor for the LiCl runs to protect reactor walls from pitting. Acetic acid to loblolly pine mass ratio was varied as 0 g, 0.2 g, 0.4 g, 0.6 g, and 0.8 g of acetic acid to 1 g of loblolly pine. Lithium chloride to loblolly pine mass ratio was either 1 g or 2 g of LiCl to 1 g of pine. For the combination run, 1 g LiCl and 0.4 g acetic acid were added per 1 g of pine. After the reactants were loaded, the reactor was purged with nitrogen for 10 min to remove oxygen. Heating time from room temperature to 180 °C required about 20 min, while four more minutes were required to heat the reactor to 200 °C. In all, reactor temperature remained above 180 °C for 19 min or above 200 °C for 15 min. The glass liner did not significantly affect the heating rate. Reaction time was 5 min after the set point of 230 °C was reached, after which the reactor was rapidly cooled by immersion in an ice bath. After immersion, the internal reactor temperature cooled to room temperature in about two and a half minutes at a rate of approximately 2 K/s. The temperature of the reactor was held at 230 °C using a PID controller. Adaptive control was necessary to maintain temperature at 230 °C in runs with LiCl. The reactor pressure was not controlled. For the runs without LiCl, pressure corresponded to the saturated vapor pressure. Each experiment at the different acetic acid and LiCl levels was performed at least three times.

2.5. Quantitative measurement of reaction products

After cooling the reactor to 25 °C, the gas product was released without further evaluation. The liquid portion and the wet solid product were separated by vacuum filtration using a Buchner funnel with Whatman filter paper (Grade 3, 0.6 μm). In the experiments with acetic acid, 1.9 g washing water per g loblolly pine was added for enhanced recovery from the reactor. If LiCl was added, 14.3 g washing water per g loblolly pine was added to ensure that the LiCl was removed from the solid product. The wet pretreated solid was dried at 105 °C for 24 h.

2.6. Analyses

The pH of the liquid portion was measured using a digital probe. Differences in pH among runs with the same reaction conditions were ±0.02 for acetic acid experiments, but as high as ±0.05 for experiments involving LiCl, probably due to acid error, a time dependent phenomena (McCarty and Vitz, 2006).

Ash analysis in triplicate was performed on all solid samples in which LiCl was added to the reactants. After drying for 24 h at 105 °C, 1 g of the pretreated solid was heated to 575 °C in a muffle furnace and maintained at that temperature for at least 12 h to ensure that only ash remained. Samples were cooled to room temperature in a desiccator before being re-weighed to determine ash percentage (Ehrman, 1994). For the acetic acid only 230 °C treatments of loblolly pine, ash was considered to be 0.4% (Yan et al., 2009).

Heats of combustion (HHV) for both raw loblolly pine and pretreated solid product were measured in a Parr 1241 adiabatic oxygen bomb calorimeter fitted with continuous temperature recording. Samples (0.2 g) were dried at 105 °C for 24 h prior to analysis. HHV values were adjusted to give values on a dry basis for raw loblolly pine.

For solid samples, fiber analysis was carried out using a modified Van Soest method using the ANKOM A200 Filter Bag Technique (Goering and Van Soest, 1970). Solid product samples (0.5 g) of approximately 0.589 mm in diameter were dried at 105 °C for 24 h. After placement in sealed filter bags, samples were digested with neutral detergent to determine neutral detergent fiber (NDF). Digestion with 1 N sulfuric acid detergent determined acid detergent fiber (ADF), and subsequent digestion in 72% sulfuric acid gave a value for acid detergent lignin (ADL). The weight percentage extracted by neutral detergent (NDF) is called water extractible. The difference of the NDF and ADF percentage yields the percentage of hemicelluloses, while ADF–ADL gives the percentage of cellulose. The weight remaining after the ADL procedure is considered to be lignin plus ash. Error in component percentages for samples without LiCl is approximately ±0.5%. If LiCl is added, error is probably an order of magnitude greater, due to interaction of LiCl with the digesting solutions.

High pressure liquid chromatography (HPLC) was performed on the liquid product of hydrothermal carbonizations at each acetic acid level. The HPLC system (SHIMADZU, CA, USA) consisted of a system controller (SCL-10A), a liquid pump (LC-10AD), a refractive index detector (RID-6A), an auto-injector (SIL-10AD), and a column oven (CTO-10A). The HPLC system was controlled by a computer running SHIMADZU EZStart software.

Operating conditions were as follows: the chromatographic separation was performed on a BIO-RAD HPLC organic acid analysis column (Aminex® HPX-87H Ion Extrusion Column, 300 mm × 7.8 mm). The column oven temperature was set at 65 °C. The mobile phase consisted of ultra-pure water containing 0.005 mol L^{-1} sulfuric acid. The flow rate of the mobile phase was set at 0.6 mL min^{-1} and the injection volume of the auto-sampler was 50 μL.

Identification of organic acids (acetic acid, formic acid, and lactic acid) was made by comparison of their retention times with those of pure standard solutions. Quantification was performed on the basis of linear calibration plots of peak area against concentrations. Calibration lines were constructed based on five concentration levels of standard solutions. Dilution of samples was necessary if the concentrations of organic acids were out of the range of concentrations shown on calibration lines.

3. Results and discussion

3.1. Lithium chloride effect on reaction pressure

Pressure of the standard reaction with no additives is approximately 4.6 MPa gauge at 260 °C, and 2.6 MPa gauge at 230 °C. These pressures correspond to the vapor pressure of water, and are largely unaffected by the presence of biomass. With the addition of 1 g of LiCl per g pine, gauge pressure at 230 °C is reduced to 1.8 MPa, while 2 g of LiCl per g pine reduces the reaction gauge pressure to 1.2 MPa. Zeng et al. (2006) describes the vapor pressure of aqueous LiCl at high temperatures, which is substantially reduced compared to pure water. Lowering the pressure of the process improves the safety of the operation, and allows for the use of less expensive reactor vessels, with decreased capital costs.

3.2. Mass yield variation with acetic acid and lithium chloride levels

Mass yield is defined as the mass ratio of dried pretreated solid to dried biomass. Fig. 1 shows the effect of acetic acid level on mass yield. Although adjacent levels may not be statistically different, the downward trend is clear. The addition of greater amounts of acetic acid results in decreased mass yield. As discussed below, more cellulose has been reacted, indicating a greater extent of reaction with the addition of higher acetic acid levels. Acetic acid has been suggested to perform a catalytic role in hydrothermal

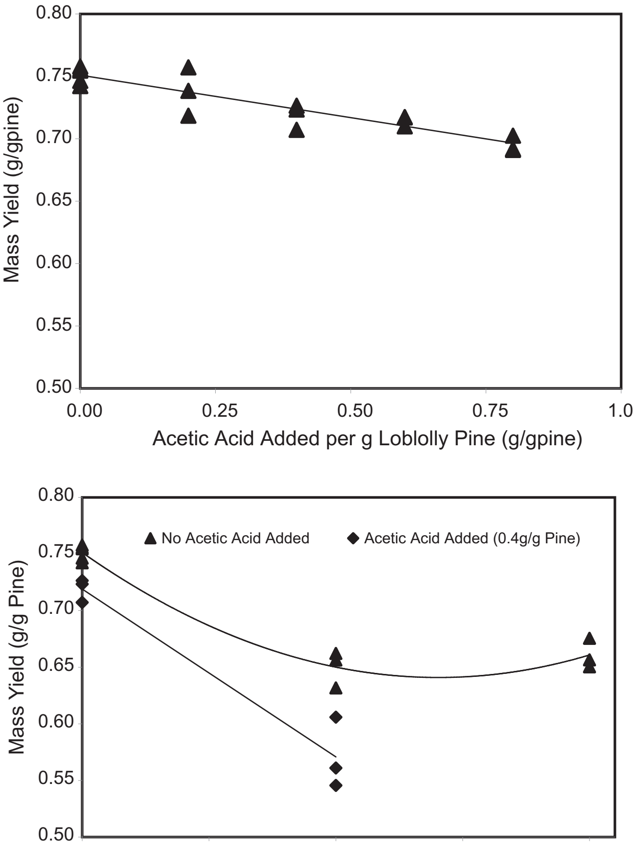

Fig. 1. Effect of acetic acid and lithium chloride addition in hydrothermal pretreatment on mass yield of solid product.

carbonization (Xu and Thomsen, 2009). When fructose is used as a model compound for biomass and hydrothermal carbonization at 220 °C is performed, a higher rate of decomposition of fructose is achieved with an acetic acid addition of 0.05 g per g fructose, suggesting that activation energy was decreased (Li et al., 2009). Higher levels of acetic acid addition likely increase severity of reaction, similar to a temperature increase. Increasing reaction temperature has been shown to decrease mass yield. For loblolly pine, at a reaction temperature of 200 °C, mass yield is 88.7%, decreasing to 70.6% at 230 °C, and 57.0% at 260 °C (Yan et al., 2009).

When an aqueous solution of LiCl is used in hydrothermal carbonization, greatly reduced mass yield results (Fig. 1). Lithium chloride has been used in combination with N,N-dimethyacetamide to decrease the crystallinity of cellulose by disrupting the strong, water-mediated H-bonding of the polymer chains (Marson and El Seoud, 1999). The cellulose crystal has been shown to change structure from cellulose I to cellulose II, a less crystalline form, in hot compressed water treatment at temperatures over 200 °C and to decompose completely above 300 °C (Kobayashi et al., 2009). Lithium chloride likely performs a catalytic role in the process (Kawamoto et al., 2008), lowering the activation energy necessary for structure change and decomposition of cellulose. Looking at fiber analysis data indicates that the percentage of cellulose, typically 54.0% for loblolly pine (Yan et al., 2009), is greatly reduced when LiCl is added to the process compared to the control (Fig. 2). Increasing the level from 1 g to 2 g LiCl per g pine does not cause further mass yield decreases. When both acetic acid and LiCl are added to the initial reaction solution, mass yield is reduced still further (Fig. 1). At 230 °C, the combination of optimal amounts of acetic acid and LiCl produces a mass yield even lower on average than that produced at a reaction temperature of 260 °C. Obviously, an additive effect from the two components exists leading to the further decreased mass yield. Adding LiCl to acetic acid reduces pH, indicating that the activity of the acetic acid has been enhanced. This effect may partially explain the greatly reduced mass yield.

When certain substances are added to water the dielectric constant decreases, making the pretreatment solvent more effective for non-polar substances. For example, at 25 °C, the dielectric constant of water is 78.46 (Uematsu and Franke, 1980). For a mixture of water with 0.045 mol fraction acetic acid, a slightly lower level than that used in the 0.8 g acetic acid per g biomass experiments, the dielectric constant is 73.2 (Kaatze et al., 1991). Adding LiCl to water also decreases the dielectric constant. In aqueous LiCl solutions with concentrations greater than 4 M, the dielectric constant would be expected to be lower than 50 (Kalcher and Dzubiella, 2009). This large and probably additive effect on dielectric constant may increase the extent of reaction.

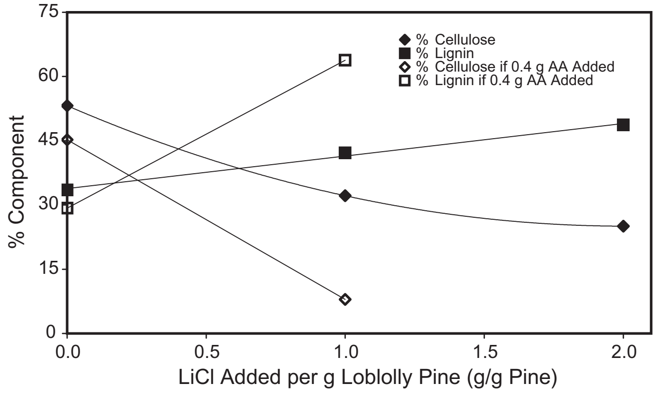

Fig. 2. Effect of LiCl addition in hydrothermal pretreatment on cellulose and lignin content in solid product.

3.3. Higher heating value variation with acetic acid and lithium chloride levels

Fig. 3 shows the effect of acetic acid level on heat of combustion. The average HHV of raw loblolly pine is 19.9 MJ/kg. The addition of acetic acid at any level increases the HHV of pretreated biomass. A maximum in HHV is found at the 0.4 g acetic acid added per g loblolly pine level. A significant increase in HHV results from adding 1 g of LiCl per g pine, with a slight possible further increase when 2 g of LiCl per g pine is added (Fig. 3). Again, an additive increase in HHV is noted when 0.4 g acetic acid per g pine is added combined with 1 g of LiCl per g pine, with HHV 30% higher than that of a run with no additives. The HHV of the combination at 230 °C is the same as that at 260 °C with no additives. Therefore, the same solid fuel could be produced at lower temperature and pressure, reducing costs of the process and improving safety. However, a glass lining for the reactor would be required because the chloride ion in LiCl could cause pitting. To combine the effect of both lithium and acetic acid addition without adding chloride ions, it is possible that lithium acetate could be useful in the process.

To explain this higher heating value data, the changes in biomass composition produced by the hydrothermal carbonization process must be examined. Biomass consists of five main components: hemicelluloses (pentosans), cellulose, lignin, aqueous solubles, and ash. Loblolly pine in particular has been measured by fiber analysis to have 11.9% hemicelluloses, 54.0% cellulose, 25.0% lignin, 8.7% aqueous soluble, and 0.4% ash (Yan et al., 2009). At 230 °C in any hydrothermal carbonization reaction, the hemicelluloses are to a great extent solubilized (Yan et al., 2009; Yan et al., 2010). Fig. 4 shows the variation of the percentages of cellulose, lignin, and aqueous solubles when different levels of acetic acid

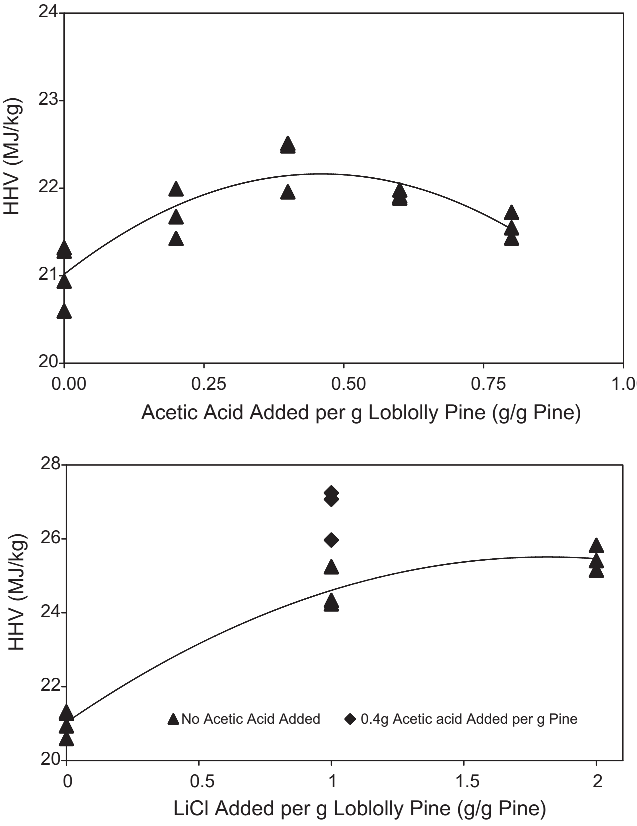

Fig. 3. Effect of acetic acid and lithium chloride addition in hydrothermal pretreatment on higher heating value (HHV) of solid product. The HHV of untreated loblolly pine is 19.9 MJ/kg.

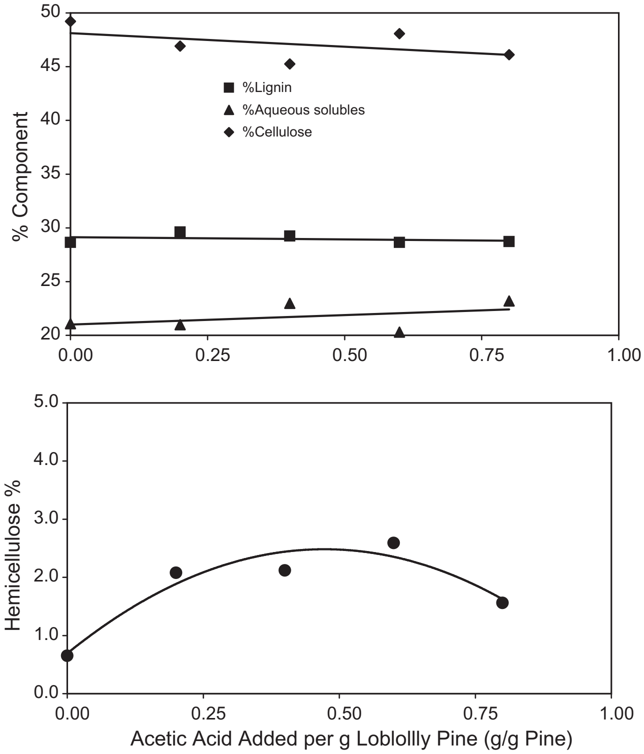

Fig. 4. Effect of acetic acid addition in hydrothermal pretreatment on fiber analysis of solid product.

are added. Increasing reaction temperature has been shown to progressively remove more cellulose from the solid product, as well as to increase HHV. For example, for loblolly pine, at a reaction temperature of 200 °C, the percentage of cellulose has been measured to be 47.4%, decreasing to 44.1% at 230 °C, and 33.9% at 260 °C. In the same study, HHV is increased from 21.12 MJ/kg at 200 °C to 22.09 MJ/kg at 230 °C to 26.55 MJ/kg at 260 °C (Yan et al., 2009). Removal of cellulose appears to correlate with increased HHV. The 0.4 g added acetic acid per g pine level has the lowest cellulose percent indicating that the highest possible HHV might be expected (Fig 4).

With increasing reaction temperature, higher percentages of lignin and aqueous solubles were found from fiber analysis, suggesting that higher percentages of these components may increase HHV (Yan et al., 2009). Looking at Fig. 4, lignin percentages appear to be fairly constant, although the 0.2 g and 0.4 g added acetic acid per g pine may be slightly higher. Both cellulose and hemicelluloses are reported to have a HHV of 17.58 MJ/kg, and lignin's HHV is 23.32 to 26.63 MJ/kg (Demirbas, 2005). Increasing acetic acid levels cause more cellulose to be reacted, possibly increasing the HHV of the solid product because a greater proportion of lignin remains. However, since the changes in lignin content are small (Fig. 4), investigating differences in aqueous solubles is appropriate. Aqueous solubles are considered to be liquid product precipitating onto the pores of the solid product (Yan et al., 2009). At a 230 °C reaction temperature, the composition of the liquid product's precipitate has been determined to be primarily 5-hydroxmethyl furfural (5-HMF) and glucose. Production of HMF has been shown to increase with increasing levels of acetic acid addition to raw corn stover under hydrothermal pretreatment at 195 °C (Xu and Thomsen, 2010). If acetic acid addition causes more 5-HMF to be formed compared to glucose, more 5-HMF than glucose likely remains precipitated in the solid product's pores. The HHV of 5-HMF can be calculated from its heat of formation to be 22.06 MJ/kg (Verevkin et al., 2009), while the HHV of glucose is 15.57 MJ/kg. Thus, a greater HHV may be linked to increased 5-HMF content in and a higher percentage of the aqueous solubles. However, too high an acid level may encourage decomposition of 5-HMF to levulinic acid or formic acid, lowering the HHV (Girisuta et al., 2006).

Hemicelluloses are almost completely hydrolyzed at 200 °C in hydrothermal reaction conditions (Yan et al., 2009; Yan et al., 2010). Slightly more hemicellulose remains when acetic acid is added to the pretreatment process (Fig. 4). The data for 0.8 g acetic acid added per g loblolly pine show only slightly lower lignin and aqueous solubles percentages compared to the 0.4 g level, but a noticeably lower hemicellulose percentage (Fig. 4). Since hemicellulose has a higher HHV than the sugars to which it converts, this may account partially for the lower HHV that the 0.8 g acetic acid added per g loblolly pine level displays.

Fig. 2 shows the percentages of cellulose and lignin in the solid samples with LiCl added to the reaction solution. The percentage of cellulose in the solid product decreases substantially with LiCl addition while the percentage of lignin simultaneously increases. When a mass balance is performed on lignin, for the 2 g LiCl per g pine and the combination 0.4 g acetic acid and 1 g LiCl per g pine runs, lignin appears to be generated. In reality, lignin-like substances not dissolvable by digestion in 72% sulfuric acid are generated. Kawamoto et al. (2008) reported that LiCl has a catalytic action on the polymerization of levoglucosan. As discussed earlier in this section, lignin has a much greater HHV than cellulose and removal of cellulose is linked to higher HHV. In addition, aqueous solubles were about twice as high for runs with LiCl added compared to those with no additives. These facts likely account for the greatly increased HHV in the products with LiCl addition.

When both 1 g of LiCl and 0.4 g of acetic acid are added per g of pine, the percentage of lignin is about twice that of a standard pretreatment run with no additives (Fig. 2), which at least partially explains the large increase in HHV. With both additives, cellulose structure, as described in Section 3.2, must be so greatly disrupted that cellulose can be removed from the solid product by digestion with 1 N sulfuric acid detergent, which normally only removes hemicellulose. Otherwise, in this case, a negative value for cellulose percentage would be calculated, which is a physical impossibility, while a hemicellulose value higher than that of raw loblolly pine would be indicated. Since for the control runs with no additives and for the runs with LiCl added, hemicellulose is completely removed from the solid product, cellulose probably should be calculated in this case as NDF–ADL, rather than ADF–ADL, as discussed in Section 2.6. Thus, the cellulose percentage for 1 g of LiCl and 0.4 g of acetic acid added per g of pine would be 8%, an extremely low value. Acetic acid and LiCl apparently interact to cause increased conversion of cellulose in the process. While higher heating value and mass reduction of hydrothermal carbonization's solid product are emphasized in this study, higher levels of conversion of cellulose to glucose in the liquid product may be helpful in further conversion by fermentation to bioethanol. Alternatively, if the glucose further reacts to form 5-HMF, 5-HMF may be converted to 2,5-dimethylfuran, a biofuel with an energy density greater than that of ethanol.

3.4. Energy densification and energy yield change with acetic acid and lithium chloride levels

Energy densification ratio is defined as the ratio of the HHV of dried pretreated solid to the HHV of dried biomass. The HHV of dried untreated loblolly pine was measured to be 19.9 MJ/kg. The energy densification ratio at a reaction temperature of 230 °C varied from 1.06 with no acetic acid addition to a maximum of 1.12 for 0.4 g acetic acid added per g loblolly pine. The addition of lithium chloride resulted in an energy densification ratio of 1.22 for 1 g and 1.28 for 2 g LiCl per g pine. Adding both 0.4 g acetic acid and 1 g LiCl per g pine gave an energy densification ratio of 1.34, increasing the heating value of the solid fuel by 34% compared to the original biomass.

The energy yield is defined as the mass yield times the energy densification ratio and indicates the total fuel value of the product solid relative to the fuel value of the original biomass. Fig. 5 shows the energy yields at the different reaction conditions. As determined by single factor (one way) ANOVA analysis, there was no statistical difference among energy yields with or without additives, except when 0.8 g of acetic acid or 2 g LiCl per g pine was added. When 0.8 g of acetic acid per g pine was added, energy yield was decreased ($p < 0.05$). Mass yield in this case was lower than that without additives, and HHV was similar, causing a lower energy yield (Figs. 1 and 3). For the 2 g LiCl per g pine runs energy yield was higher ($p < 0.05$), due to the slight decrease in mass yield and the substantial increase in HHV compared to those for the runs with no additives (Figs. 1 and 3). For all the other cases, including the one where both 0.4 g of acetic acid and 1 g LiCl per g pine was added, energy yield was the same at 0.8. Of the original energy contained in the raw biomass, 80% remained in the pretreated solid product. Even though mass yield was decreased with increasing acetic acid addition and with the addition of lithium chloride, due to increased energy densification ratio, the energy yield stayed high. Adding acetic acid and/or lithium chloride does no harm to energy yield, unless levels higher than 0.6 g acetic acid per g pine are used.

3.5. Final pH change and concentration change with acetic acid and LiCl addition

Fig. 6a shows the pH values of the liquid product of the hydrothermal carbonization process when varying amounts of acetic acid were added. These values were measured after 1.9 g of washing water per g loblolly pine was added to the final product. As expected, addition of more acetic acid reduces the pH, causing more severe reaction conditions. When no acetic acid is added to the initial reactants, 0.03 g of acetic acid is produced per g original pine (Yan et al., 2010). This quantity, diluted in 5 g initial water plus 1.9 g washing water, should result in a solution with the calculated pH of 2.95. This concurs with the measured value. However, if 0.4 g acetic acid is added to the 0.03 g acetic acid expected to be produced, with the same amounts of water added, a pH of 2.39 would be expected. This expected value is significantly lower than the measured value of 2.61. Similar results are found for all levels of addition of acetic acid.

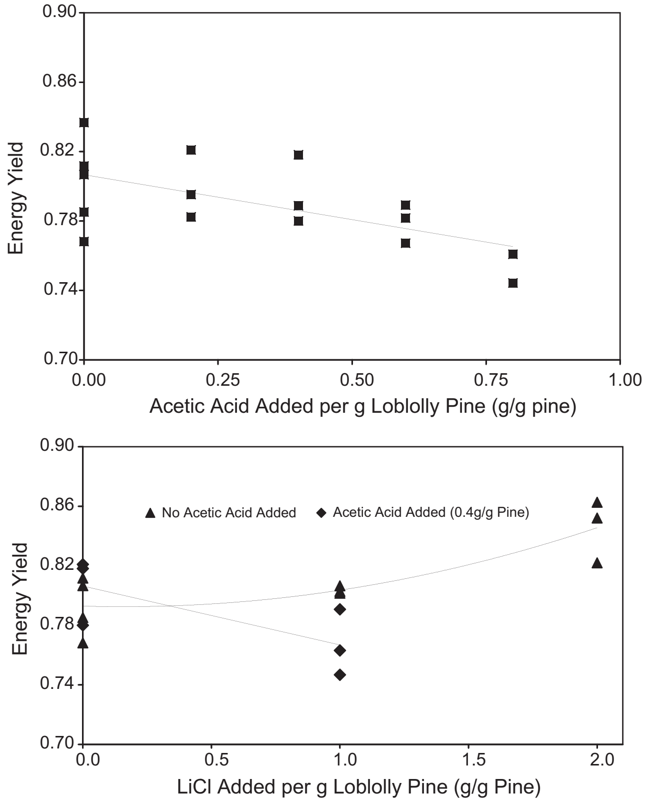

Fig. 5. Effect of acetic acid and LiCl addition in hydrothermal pretreatment on energy yield (product of mass yield and energy densification) of solid product.

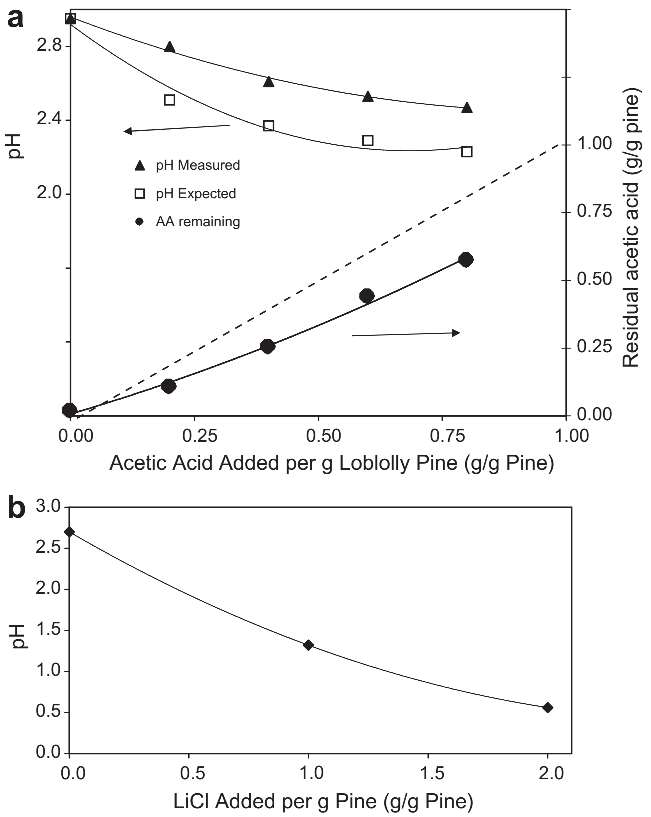

Fig. 6. (**a**) Effect of acetic acid addition in hydrothermal pretreatment on the pH of the liquid product. See text for complete description. Also shown is the effect of acetic acid addition on amount of acetic acid per g of pine detected by HPLC in the liquid product after hydrothermal pretreatment (**b**) effect of lithium chloride addition in hydrothermal pretreatment on pH of liquid product.

One reason pH could be higher than expected is that greater amounts of water may be produced with the addition of acetic acid. Several studies have suggested that dehydration of the biomass is one of the main mechanisms for removal of O and H from the solid product to improve its fuel value. In particular, production of 5-HMF, one of the major precipitates of the process, is formed through dehydration reactions (Knezevic et al., 2010; Yu et al., 2008). Thus, one effect of acetic acid addition may be the production of water in the reaction scheme. Alternatively, when more acetic acid is present initially, reaction products produced in greater amounts may reduce the activity coefficient of acetic acid, causing a higher pH reading. However, looking at the actual concentration values is likely to shed more light on the unexpectedly high pH values.

The actual amounts of acetic acid in solution per g of pine after reaction as a function of added acetic level was calculated from

HPLC measurements, also shown in Fig. 6a. In all cases where acetic acid is added, no additional acetic acid is produced. When acetic acid is added, less acetic acid exists at the end of the reaction than at the beginning. Obviously, decomposition or consumption of acetic acid must occur when it is present in the reaction scheme. Acetic acid may decompose under the reaction conditions to methane and carbon dioxide. Indeed, when a control run of acetic acid solution only (without biomass) of initial pH 2.09 is subjected to 230 °C hydrothermal carbonization conditions, a release of gas and a pH rise to 2.13 is noted afterward. The same effect of acetic acid reduction is found when 0.4 g acetic acid is added per g of raw corn stover under hydrothermal pretreatment at 195 °C (Xu and Thomsen, 2010). When acetic acid is added to the reaction, the same amount may decompose while less is formed, so that a net loss of acetic acid is experienced.

One explanation for acetic acid not being produced when initially added to the process is that the reactions to produce acetic acid could be reversible reactions, with added acetic acid pushing the equilibrium in the direction of reduced acetic acid production. Glucose, a product of cellulose degradation, further reacts to form acetic acid, as well as formic and lactic acids (Yoshida et al., 2005). With addition of acetic acid, glucose may decompose to other products instead. Indeed, when 0.4 g acetic acid per g pine is added, the reaction produces more than 7 times as much lactic acid as compared to a standard run. Decomposition of hemicellulose occurs by 230 °C (Yan et al., 2010) and significant production of acetic acid is thought to result from the acetyl groups originally existing in hemicellulose molecules (Lu et al., 2009a,b; Yoshida et al., 2005). One source of acetic acid is likely acetylated galactoglucomannans, the main hemicellulose in most softwood species (Xu et al., 2010a,b). Detachment of acetyl groups from hemicellulose to form acetic acid may be a reversible reaction. If addition of acetic acid causes less acetyl groups to be removed from the hemicellulose, so that it is less reacted, more hemicellulose might be expected to remain in the final product. More hemicellulose does remain when acetic acid is added (Fig. 4). Thus, a shifting of equilibrium reactions, formation of alternative products, and decomposition of acetic acid under the altered conditions may explain the less than expected end concentrations of acetic acid and the increased pH.

The pH values of the liquid product when different levels of LiCl were added are shown in Fig. 6b. These values were measured before any washing water was added. Because pH is defined as $-\log(a_{\mathrm{H}}^{+})$ and activity equals the activity coefficient γ times concentration, γ obviously can play a major role in what pH is measured. Adding a neutral salt, such as LiCl, can decrease the pH significantly (McCarty and Vitz, 2006). In a standard reaction, about 0.03 g of acetic acid is generated per g of pine (Yan et al., 2010). In a solution containing approximately that amount of acetic acid plus 1 g of LiCl in 5 g of water the measured pH was 1.5. When 2 g of LiCl was added to a solution with the expected amount of acetic acid for a standard run, pH was 0.75. These pH values are higher than those produced in the reactions, which were 1.3 for 1 g LiCl added and 0.56 for 2 g LiCl added per g pine. Thus, when no acetic acid is added, more acid is produced when LiCl is added than is produced in the standard pretreatment. Clearly, LiCl exerts a catalytic effect in the decomposition of cellulose (Marson and El Seoud, 1999; Tosh et al., 2000) and in the production of higher levels of acid in the solution produced by the hydrothermal carbonization of biomass.

In the runs where both 0.4 g acetic acid and 1 g LiCl were added per g pine, pH at the end without washing water was 1.08. This corresponded exactly to the pH (1.09) for a solution of 0.4 g acetic acid plus 1 g LiCl in 5 g water with no biomass. Since the pH is the same, it is likely that the same amount of acid was produced as was consumed in the process. As discussed previously in this section, when acetic acid is added to the initial reaction solution, no additional acetic acid is produced and acetic acid is consumed. However, adding LiCl does cause acid production. When both are added, there is apparently no net acid production since the pH remains the same. If both 0.4 g of acetic acid and 1 g of LiCl per g pine are added to the process, HHV increases by 30% compared to the standard process, and the acetic acid level remains the same, so that the end solution could be recycled to treat new batches. Engineers with an interest in using these additives in hydrothermal carbonization must devise a separation and recycle scheme to optimize the overall efficiency of the process.

4. Conclusions

Addition of acetic acid and/or LiCl to hydrothermal carbonization of lignocellulosic biomass contributes to increased fuel density of the solid product. HHV is increased and mass yield is reduced when 0.4 g of acetic acid is added per g pine. Addition of LiCl reduces reactor pressure and increases the energy densification ratio. Added at a ratio of 1 g LiCl per g pine, LiCl addition results in greatly increased HHV and reduced mass yield. Cellulose degradation is promoted by the addition of acetic acid and/or LiCl, while energy yield is relatively independent of the additives.

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